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CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

NOTE CONCERNING THE SILVER COULOMETER.

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In a recent paper Messrs. Smith, Mather and Lowry have recounted their numerous and carefully executed experiments on the silver voltameter, or coulometer.[1] Their results are valuable, for they appear to have shown that it is possible to obtain an accurate result with the silver coulometer without the trouble of interposing either porous cup or siphon between the anode and the cathode.

One of the respects in which their experiments have differed from those of others is their use of a large volume of electrolyte. It is not surprising that this device tends toward accomplishing the desired end; for when the volume of the electrolyte is sufficiently large, the anomalous substances formed at the anode are so much diluted as to have but slight effect on the cathode. Moreover, the chance that these substances will be affected by dissolved air is much greater in the larger volume.

Although in this respect the new English work is of great service, there are one or two points in which exception may be taken to the authors' conclusions, and this note is written to call attention to these points. The coming International Meeting upon Electrical Standards renders it desirable that the matter receive promptly as much discussion as possible.

First among the minor points is the much disputed question as to whether silver crystals deposited in the coulometer contain liquid inclusions. Upon page 570 of their paper Smith and Mather speak of having attempted to test this point by reheating deposits previously dried at 160° to 240° in eight cases and to over 400° on three other

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1 Phil. Trans. Roy. Soc. London., Series A., **207**, 545 (1908).

occasions. My own experience leads me to believe that these temperatures were not any of them high enough to effect the expulsion of the included mother liquor. The same objection applies in a smaller degree to the work of van Dijk.[2] Silver containing included mother liquor does not give up this mother liquor until the temperature has been raised to so high a point that the metal becomes somewhat softened, and then the mother liquor is set free by a series of small explosions or decrepitations. The temperature needed is probably over 600°, as may be inferred from the statements made in my previous article on this subject.[3] It is probably true that the current density and other conditions at the time of the deposit cause variations in the amount included, but I have never by any process obtained silver which did not include a trace of mother liquor. That the inclusions are not due to extraneous impurities in the silver nitrate, but really occur with the purest salt, is conclusively shown by the recent experiments of Duschak and Hulett.[4] Therefore it is clear that the weight of silver dried at 160° does not give the precise weight deposited by the current, although the amount of included mother liquor may be so constant as not to interfere with the use of the weight obtained in this way as a technical measure of current strength.

Messrs. Smith and Lowry have done good service in emphasizing the importance of using really pure silver nitrate — a precaution not always heeded by physicists. One detail of their argument does not seem to be proved, however. They state that nitric acid causes a decrease in the amount of the deposit, — a very probable effect, which might have been predicted beforehand; but this conclusion can hardly be drawn from the results which they give on page 595. When small quantities of nitric acid (corresponding to about 0.1 to 0.2 of a per cent of the amount of silver nitrate present) were added, the average of their four results showed not a decrease but an *increase* in the weight of the deposit by 7 parts in 100,000; and when as much as 1 per cent of nitric acid is present, the average deficiency was only 4 parts in 100,000 as an average of seven experiments showing a rather large probable error. One would therefore be inclined to infer on the basis of their experiments that a small amount of nitric acid has no effect — or at least a much smaller effect than they are inclined to ascribe to it. One finds it difficult to agree with their conclusion on page 596:

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2 Van Dijk and Kunst, Ann. der Phys., **14**, 569 (1904); Van Dijk, ibid., **19**, 249 (1906).

3 These Proceedings, **37**, 435 (1902).

4 Trans. Am. Electrochem. Soc. (1908).

"We conclude, therefore, that whilst the abnormally low values which are observed from time to time can only be explained by the presence of acid, it may be very difficult in practice to add nitric acid without at the same time introducing other impurities which may more than counterbalance the effects produced by the acid itself." [5]

To this supposed influence of nitric acid they ascribe the fact that on thirteen occasions they found less silver in the experiments where a porous cup was interposed between the anode and the cathode than where the cup was absent. They infer that the porous cup was not adequately washed from nitric acid. This is possible, although it seems more probable that, as they suggest, cyanide, which is notoriously difficult to wash out of porous material, was the real cause of the deficiency, as indeed they suggest on the third line of page 564. They obtained good results when their porous cups were ignited for some time in an electric furnace. This treatment would drive off not only nitric but also hydrocyanic acid, and might oxidize any remaining cyanide.

To sum up the last paragraph: it may be pointed out that there is little evidence presented that nitric acid, if present in traces, would have produced a deficiency in the silver deposited, and some doubt as to whether nitric acid was present in the experiments of Smith, Mather and Lowry with porous cups. Hence the conclusions of those gentlemen concerning the unsatisfactory behavior of their insufficiently washed cups are of doubtful value. Nevertheless it would obviously be well in future work to make sure that nitric acid is wholly absent, and they have done a service by calling attention to the danger of incomplete washing of the porous cell if that is used. It is not probable that this difficulty affected the determinations made at Harvard, because cyanide was not used for washing the cells, and, as is stated in one of the papers,[6] the solution around the cathode in our cases remained wholly neutral. Moreover, in the Harvard experiments the porous cup method was compared with another method free from any possible defect of this kind, and found to give the same result.[7]

One other point may be mentioned in which the results of Messrs. Smith, Mather and Lowry differ from the Harvard results. The English experimenters were unable to find that freshly formed anode liquid

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[5] Professor Smith, in a letter kindly written after he had seen the manuscript of the present note, explains that there was some doubt as to the purity of some of their nitric acid. This doubt may have applied equally to that used in washing their porous cells, however.

[6] These Proceedings, **35**, 141 (1899).

[7] These Proceedings, **37**, 420 (1902).

deposited silver upon contact with the silver surface. This is a crucial experiment, and the result is purely a question of fact, not of interpretation. Clearly for some reason or other the anode irregularities were less prominent in the experiments of Smith, Mather and Lowry than in other cases, and one is inclined to refer the difference in this respect between the results which they obtain and the Harvard results to other causes as yet unknown. Possibly the fact that they used electrically deposited silver for their anode may not only account for their inability to deposit silver from the heavy anode liquid, but also contribute toward the constancy of their results with Lord Rayleigh's voltameter. Electrically deposited silver, being arranged in definite crystals, may dissolve with less irregularity than a fused lump. Further experiments must decide the uncertainty. For the present, until this question has been settled, it would seem to be advisable to use electrically prepared silver as the anode, if a porous cup is not employed.[8]

It is to be hoped in view of these points still remaining unsettled that the International Congress on Electrical Standards will not define too positively the true electro-chemical equivalent. It is equally obvious that with the exception of these disputed points the matter is in a much more definite state than it was twenty-five years ago. There can be no doubt that the final result of Lord Rayleigh and Mrs. Sidgwick was the best of all the early absolute determinations, all things considered, because of their having taken account of the inclusion of mother liquor. In this respect this pioneer work is better even than some of the most recent work. Probably it was not over 0.05 per cent in error — a remarkable degree of accuracy for that time.

In brief, the contents of this note may be summarized as follows. While it is clear that Smith, Mather and Lowry have done good service in showing that large volumes of liquid, taken in connection with the electrically prepared anodes, will give good uniform results with the silver coulometer, and that the results thus obtained are like those obtained with clean porous cups and siphons between the electrodes, there are still a few minor points of detail left to be decided, especially the question as to the amount of included liquid in the silver.

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[8] I am glad to hear from Professor Smith that the National Physical Laboratory of England proposes to test this and other doubtful points in the near future.